Study on Rheological Properties of Sodium Carboxymethyl Cellulose in the presence of mixed surfactants and Electrolytes

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Under the Guidance of

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CERTIFICATE

This is to certify that the project report entitled, **"Study on Rheological Properties of Sodium Carboxymethyl Cellulose in the presence of Mixed surfactants and Electrolytes"** submitted by **Chinmaya Mishra (710CH1141)** in partial fulfilment for the requirements for the award of Dual Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

The effect of mixed surfactant systems of CTAB (cationic) and IGEPAL – CO 890 (non ionic) as well as different electrolytes i.e. NaCl, Na_2SO_4, and NaH_2PO_4 on the flow rheological properties of CMC has been studied. Initially various properties such as CMC values, surface excess, β interaction parameter and area of the molecule are calculated for mixed surfactant systems in the ratio of 7:3 and 3:7 (CTAB to IGEPAL CO -890) and also in the presence of electrolytes at 150mmol at low value of mixed surfactants. Low values of CMC were observed for mixed surfactant systems due to higher synergistic effect and minimum surface tension value is also low for the mixed surfactant solution compared to that of the pure surfactants. Later flow rheological properties of carboxymethyl cellulose i.e. change in viscosity and shear stress for a wide range of shear rate in the presence of surfactants and electrolytes were observed. It was observed that at low shear rate viscosity values were higher and with increasing shear rate the values decreases. It was also observed that with increase in surfactant values and valency of electrolytes the shear stress decreases due to adsorption of surfactant molecules in between the polymer molecules which results in disruption of the structured molecules.

Keywords: Carboxymethyl Cellulose, Mixed Surfactants, Critical Micelle Concentrations, CTAB, IGEPAL CO -890, Rheology, Electrolytes.

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NOMENCLATURE

CMC	Critical Micelle Concentration
CTAB	Cetyltrimethylammonium bromide
NaCl	Sodium Chloride
NaH_2PO_4	Sodium Phosphate
Na_2SO_4	Sodium Sulphate

LIST OF SYMBOLS

Γ	Surface excess concentration
β	Interaction Parameter
A	Area covered by one molecule in a surface layer
A_{in}	Hysteresis Area
R	Universal gas constant
T	Temperature
γ	Surface tension
N_o	Avagardro's Number

Chapter 1

INTRODUCTION

INTRODUCTION

1.1 Rheology

Rheology is a branch of mechanics which includes the study of those properties of materials which respond to the mechanical force applied on them. It typically deals with non-Newtonian fluids and the plastic flow of solids and their deformation due to various forces acting on them. Extremes of rheological behaviours as follows:

ELASTIC behaviour - e.g. perfectly rigid solids - where any deformation reverses spontaneously when an applied force is removed. Energy is stored by the system, then released.

VISCOUS (or PLASTIC) behaviour - e.g. ideal Newtonian liquids – it is a type of behaviour where any deformation which has occurred to the body ceases as soon as the applied force is removed. Energy performs work on the material.

The real world of most substances lies between this elastic and viscous behavioural range which are termed as viscoelastic materials. Rheological studies generally interprets the behaviour of non-Newtonian fluids, by defining the lowest possible ways that are required to relate stresses with rate of change of strain or strain rates. For example, the viscosity of ketchup gets reduced by shaking (even when it includes any form of other mechanical agitation or stirring, where the reduction in viscosity is caused by the relative movement of different layers in the fluid). Ketchup is a shear thinning material, like yoghurt and emulsion paint (US terminology latex paint or acrylic paint), exhibiting thixotropic properties, where an increase in relative flow velocity will cause a reduction in viscosity, for example, by stirring. Shear thickening or dilatant materials are those Newtonian fluids whose viscosity goes up with relative deformation and hence shows opposite behaviour than shear thinning materials.

1.2 Importance of Rheology

Nowadays, there are many fundamental and applied dynamics process for which the characterization of adsorbed interfacial layers of surfactant and polymer molecules is very essential. These contain foaming and emulsification that are widely used in the production of cosmetics, pharmaceuticals and food, mining, oil industry, etc. Understanding the mechanism of surfactant adsorption at the fluid interface is a central proposal in the knowledge of their

functionality and applications. Currently there is a significant interest in industrial applications, studying dynamics of interfacial layers. These studies are much useful in understanding the interaction between molecules, change of molecular conformation or molecular aggregations. Currently rheology also plays a much important role in food product design. In liquid fluids this branch generally deals with the microstructural level of liquid foods which determines its quality as well as quantity. The study on microstructures provides us with a lot of information regarding the concept behind the physic-chemical bonds and inter or intra molecular associations between the ingredients in any mixture. Microstructure associates fundamentally with the flow characteristics of a material, for example, viscosity and elasticity that is much important in heat and mass transfer. Principally rheology concerned with extending continuous mechanics to characterize the flow of material, which contain a combination of elastic, viscous and plastic behaviour by applying elasticity and fluid mechanics. At the micro- or Nano structural level of the material e.g. the molecular size and architecture of polymers in solution the study of rheology helps in predicting the mechanical response. Materials with the characteristics that of a fluid will show changes in its fluidic properties when subjected to the stress that is force per unit area. There are different types of stress (like shear, torsional, etc.), and materials can respond differently to different pressures. Theoretical rheology is much concerned with external forces and torques with internal strain gradients and flow velocities.

Rheology combines the seemingly unrelated fields of plasticity and non-Newtonian fluid dynamics by recognizing that materials undergoing these types of deformation are unable to support a stress in static equilibrium. So, a solid undergoing plastic deformation is a fluid. Rheology also helps to establish the relationships between deformation and stresses, by correct measurements.

1.3 Mixed Surfactants System :

The studies on surfactant mixtures have been done from the viewpoints of molecular-molecular interaction as well as of their many practical applications on our day to day life. Generally a mixed surfactant system is either of the combinations of an ionic and non-ionic surfactants. Mixtures of ionic and non-ionic surfactants, electrolytes, dyes and fillers etc. are the typical compositional elements of industrial surfactant. Some of these species are mixed with the single surfactant in order to obtain higher synergistic effects and others to control ionic strength, pH, viscosity and other physicochemical properties of the system. Hence,

desirable surface properties for specific applications can be obtained by adjusting the compositions of these systems. However, to choose an appropriate surfactant system requires an understanding of the adsorption phenomena in these systems as well as the interactions between molecules adsorbed at the interface. In other words, a theoretical model of the adsorption process in mixed systems is required. It was observed from previous studies that the polar head group of non-ionic surfactant attracts inorganic cations in adsorbed films and micelles and a large difference in the size of head group between ionic and non-ionic surfactants is favourable for the packing of the surfactants, and a counter ion with a large hydration radius is less effective than that with a small hydration radius for the shielding of the charge on the ionic head group of surfactant in adsorbed films and micelles and causes large interaction between the head groups of ionic and non-ionic surfactants**.**

1.4 Importance of Mixed Surfactants:

Mixed surfactant systems arise from various sources and are almost found in every other practical application of surfactants. Firstly, it results due to impurities in initial materials and incongruences in the products obtained in reactions during their manufacture. These mixed systems are basically cheaper to produce than isomerically pure surfactants and often provide quite better desirable results. Secondly, to enhance the synergistic behaviour in mixed surfactants or to obtain qualitatively varied types of performance in a single formulation (e.g. cleaning plus fabric softening). Finally, in order to control or improve the physical properties of the system or just to enhance its stability, these system of surfactants are generally added to the practical formulations.

1.5 Critical Micelle Concentration analysis of Mixed surfactants :

Whether it is an isomerically pure surfactant or the mixtures of the pure ones, they exhibit a wide range of beneficial and interesting phenomena. It was observed that at low concentrations of surfactant solution in water, significant changes in the properties at the interfaces were observed. The most pronounced effect is the lowering of interfacial tension due to preferential adsorption of surfactant molecules at solution interfaces. The decrease in surface tension becomes linear with increasing surfactant concentration, gradually becomes linear with the logarithm of the concentration of surfactants and monolayers or bilayers of surfactant molecules at the solution interfaces. The decrease in surface tension reaches an ultimate value after which there is no further decrease is observed. At this surfactant concentration micelles start to form which is generally termed as micellization and the

concentration is called as critical micelle concentration (CMC). At this CMC value, the surfactant molecules undergo cooperative aggregation process to form large surfactant micelles with the hydrophobic part of the molecules facing to the interior of the aggregates and the hydrophilic head groups heading towards the surface in contact with aqueous solution. This process could occur both ideally and non-ideally mixing. Randomly mixed surfactant aggregates will tend to form as the hydrophobic effect drives the overall process is not specific to a particular surfactant "head" group this mixing process can be described as the "ideal" component of mixing in the aggregate. In the case of mixtures with different surfactant types, electrostatic interactions between "head" groups can provide the basis for the "non-ideal" component of mixing in the aggregate.

A mixed surfactant system forms due to the mixture of two surfactants and it's mixed CMC (C^*) values are given by the equation, C^*

$$\frac{1}{C^*} = \frac{\alpha_1}{f_1 C_1} + \frac{(1-\alpha_1)}{f_2 C_2} \quad (1)$$

Where $\boldsymbol{\alpha}_1$ is the mole fraction of first surfactant in total mixed solute, f_1 and f_2 are the activity coefficients of first and second surfactants, respectively, and C_1 and C_2 are the CMC of pure surfactants. In ideal case $f_1 = f_2 = 1$; hence equation (1) becomes,

$$\frac{1}{C^*} = \frac{\alpha_1}{C_1} + \frac{(1-\alpha_1)}{C_2} \quad (2)$$

For mixed surfactant system, CMC can be determined by surface tension concentration curves. Along with surface tension, CMC can also be measuring by micelle influenced property such as electrical conductivity, light scattering, pulse radiolysis, density, viscosity and refractive index.

Chapter 2

LITERATURE SURVEY

2.1 Previous Studies on Mixed Surfactants

The studies on mixed surfactants recently has shown growing interests in different area such as pharmaceuticals, oil recovery industry, environmental as well as Nano Technology. The role of mixed surfactant systems totally depends on its CMC values, their surface properties and how well different surfactant molecules interact with each other. Hence to understand their behaviour a depth research on their physicochemical properties is needed.

Table 2.1 Previous studies on CMC of mixed surfactants.

Mixed surfactants system	**Characterization Parameters**	**Applications**	**Reference**
N,N'-bis(dimethyldodecyl)-1,2 ethanediammoniumdibromide (12-2-12) and N,N'-bis(dimethyldodecyl)-1,4-butanedi-ammoniumdibromide (12-4-12)	Surface Tension, Phase behaviour test, surfactant-surfactant interaction in micelles	Enhanced oil recovery	Parekh et al
SDS (Anionic) and Polyoxyethylene (Nonionic)	Surface Tension, Conductivity.	Food Grade Emulsions	Yow-Lin et al
Nonylphenol polythoxylate (Nonionic) and Sodium dodecyl sulfate (Anionic)	Surface tension	Food Grade Emulsions	Li-Jen Chen et al
Tetradecylpyridinium bromide (Cationic) and Triton-X-100 (Nonionic)	Surface tension	Phase behaviour	Parihar et al
N-N dimethyl-N-lauroyl lysine (Amphoteric) and Sodium dodecyl sulfate (Anionic) and inorganic electrolytes.	Surface tension, pH, relative viscosity	Food grade micro emulsions	ABE et al
SDS (Anionic) and CTAB (Cationic)	Pyrene intensity ratio	Iron nanoparticles production	Alargova et al
CTAB (Cationic) and Triton-X-100 (Nonionic) with Sodium Bromide.	Surface Tension, EMF measurements.	Cosmetics and Drugs	Javadian et al

The above studies qualitatively shows the study on the CMC values of mixed surfactants and how they vary in comparison to individual surfactants. The superior properties of mixed surfactants can be used to low down the production cost. Javadian et al. investigated the effect of electrolyte on CMC of mixed surfactants in an industrial scale as one confront with various types of surfactant as well electrolyte systems in the whole operational units basically related to cosmetic and drug. ABE et al explained the adsorption phenomenon in these systems. As ABE et al. studied the effect of inorganic electrolytes and pH on a mixed micelle formation of amphoteric and anionic surfactant system in terms of surface tension, pH and relative viscosity.

Parekh et al. studied the mixed surfactant systems of (SDES) and Gemini surfactants (cationic) at different molar concentration ratios by finding out the relationship between the surface tension values and the required molar concentrations required to attain the CMC value of the mixed surfactant system at standard condition. Parameters like CMC, surface excess concentrations, minimum area per molecule, and interaction parameter of mixed micelle have been studied using different approaches. Alargova et al spontaneously investigated the critical micelle concentration and micelle aggregation number of various conventional surfactant and dimeric anionic and cationic surfactants by electrical conductivity, spectrofluorometry. Simultaneously he carried out the effect of mixture composition on the mixed micelle aggregation number. Also, Alargova compares non-ionic conventional surfactant with ionic surfactant. Parihar et al. also studied mixed micellization process of binary mixtures formed by surfactants. Also, he examined the mixed CMC values by surface tension method to gain the same effect for the combination with synergism than without synergism and phase behaviour.

2.2 Rheological Studies of CarboxyMethyl Cellulose:

In a current industrial scenario, it's quite essential to learn the uses of Carboxymethyl cellulose as well as the effect of various additives on its rheological properties. A number of studies have been done on CarboxyMC with different additives to find out rheology and its effect on the emulsion. Currently CMC has number of applications like thickening and dewatering of mineral slurries, paint manufacture, cosmetics industry. So, in order to get better synergism with those additives many researchers investigated the effects of polymer, surfactants as well as electrolytes on it.

Table 2.2 Previous studies on rheological properties of CarboxyMethyl Cellulose

System	Rheological Parameters	Applications	Reference
Different concentration of Carboxymethyl Cellulose.	Shear Thining, Cross Modelling, Viscoelasticity	Water Based Drilling Fluids.	Karim et al
Carboxymethyl Cellulose with Cellulases	Rheological Effects.	Foods Science, textiles, Pulp and Paper	Jung et al
Carboxymethyl Cellulose of different concentrations	Flow behaviour	Paint manufacture, food chemistry.	Amiri et al
Carboxymethyl Cellulose	High temperature/pressure rheology of carboxymethyl cellulose	Cosmetics chemistry.	Abdelrahim El-Din et al
carboxymethyl cellulose (CMC) and xanthan gum (XG)	analysis of flow measurements	Polymer chemistry.	Escudier a et al
Carboxymethyl Cellulose, Cationic Surfactant and Alum	Tensile strength and tensile index	Paper recycling.	Somayeh et al
Carboxymethyl Cellulose Cationic surfactants, i.e., dodecyltrimethylammonium chloride, dodecyltrimethylammonium bromide	tensiometry, viscosimetry or ion-selective electrode method, and dynamic light scattering	Foods Sciences, Textiles.	Jitendra et al

Karim et al studied the rheology and binding mechanisms in the aqueous system with the help of rotational rheometer predicted two critical concentrations of sodium carboxymethyl cellulose solutionsr. He also studied the effect of surfactants on the viscosity as well as the internal structure of Carboxymethyl cellulose by using the methods i.e. flow curve shapes, Cross model parameters, variation of the viscosity versus the overlap parameter, and

empirical structure–properties relationships and found a transition of a strong to semi dilute network system. Jung et al. studied the effect of cellulose treatments on the Carboxymethyl Cellulose using a stress controlled rheometer and shear thinning behaviour. Amiri et al also studied the rheological properties of aqueous solution Carboxymethyl cellulose at a weight fraction of containing 0.05, 0.1, 0.25 and 0.5% of cellulose in aqueous media. Samples with lower concentration of cellulose i.e. 0.05 and 0.1 showed Newtonian behaviour but shear-thinning behaviour with increasing the concentrations to 0.25 and 0.5% as the system becomes more viscous. Abdelrahim et al studied rheological properties with the help of a digital rotational viscometer with a dynamic to and fro linear–ramp shearing sequence. Escudier et al showed that the viscosity, storage and loss moduli for carboxymethyl cellulose and xanthan gum (XG), are practically insensitive to the chemistry of the tap water used as a solvent, to the method of mixing, and to the biocide added. Somayeh et al carried out the study to determine the effect of the Carboxymethyl cellulose on recycled pulp properties produced from Old Corrugated Container (OCC). The main advantages in these experiments are enhanced tensile as well as burst strength of the hand sheets. Mata et al. examined the interaction between polymer–surfactant in mixed solutions of the cationic surfactants in water and aqueous salt solutions by tensiometry, viscosimetry or ion-selective electrode method, and dynamic light scattering. The effect of varying surfactant chain length, head group size, counterions, and ionic strength on the critical aggregation concentration (CAC) of mixed polymer surfactant systems and the collapse of the polymer molecule under different solution conditions were also studied.

Chapter 3

EXPERIMENTAL SETUP

This chapter is focussed on experimental methods and experimentation followed in the project. The surface tension measurements of mixed surfactants were done using Wilhelmy plate tensiometer at ambient conditions of temperature and pressure. The surface tension values were measured over some time using the instrument. The rheological study of individual surfactant and mixed surfactants was also done by using TA HR-2 hybrid rheometer for mixed surfactants with over define time at various modes and temperature ranges.

3.1 Materials

Cationic surfactant Cetyl trimethyl ammonium bromide (CTAB, purity >99%) and non-ionic surfactant IGEPAL CO-890 were purchased from Sigma Aldrich. Carboxymethyl cellulose sodium salt was purchase from LOBA Chemicals. The electrolytes used were sodium chloride, sodium sulphate were purchased from RANKEM Chemicals. Sodium di-hydrogen phosphate was purchased from Merck Millipore. Anhydrous Ethanol for cleaning purposes was obtained from Merck.

3.2 Properties of Chemicals Used

- **Cetyl trimethylammonium bromide (CTAB)** is one of the important cationic surfactantd which has a molecular weight of 364.5g/mol and molecular formula $(C_{16}H_{33})N(CH_3)_3Br$. It is well soluble in water and it is quite a beneficial antiseptic agent against fungi and bacteria. The CMC value of CTAB is theoretically found to be 1mmol. It has molecular structure as shown in figure 3.1.

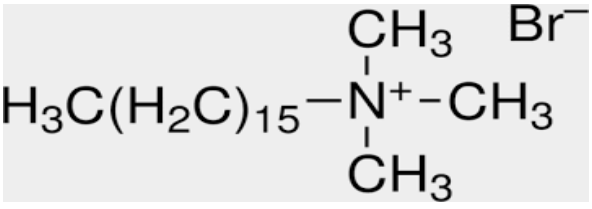

Figure 3.1 Molecular Structure of CTAB.

- **IGEPAL CO-890** is a non-ionic surfactant which has a molecular weight of 1982 g/mol and molecular formula $(C_2H_4O)_n \cdot C_{15}H_{24}O$ where n=40. It is a versatile emulsion polymerization surfactant which can be used as latex post stabilizer. It is

also used as sole-emulsifier and co-emulsifier. It has the molecular structure as shown in figure 3.2. The critical molar concentration value (CMC) value is 0.3mmol.

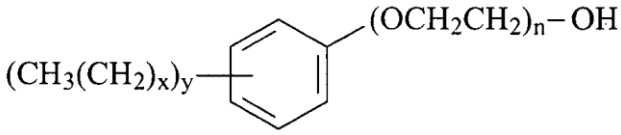

Figure 3.2 Molecular Structure of IGEPAL CO-890.

- **Sodium Carboxymethyl Cellulose** (CMC) is a derivative of cellulose containing carboxymethyl group. It behaves as an anionic polyelectrolyte and due to the presence of polar carboxyl group, it is easily soluble in water and chemically reactive. It has following functions and properties:
- It acts as a thickener, viscosity modifier binder and stabilizer in food industries such as ice creams, bakery products such as cakes and breads.
- It is used as a thickening agent in pharmaceuticals and as an important ingredient of drilling mud in oil-drilling industry.
- It forms a eutectic mixtures which helps in reducing freezing point and hence used in ice packs.

The above properties and functions of the cellulose widens the range for its use for different applications in the food, pharmaceutical, cosmetic, paper, and other industries. This cellulose is basically available in three grades: standard, food, and pharmaceutical and this classification is based on the particle size, molecular substitutions, viscosity and many other parameters.

3.3 Surface Tension Measurements:

3.3.1 Working Principle of Wilhelmy plate Tensiometer:

Surface tension measurements at air-surfactant interface were done with a Platinum Wilhelmy plate on a surface tensiometer (Dataphysics, Filderstadt, Germany, DCAT 11EC) which is shown in figure 3.3.

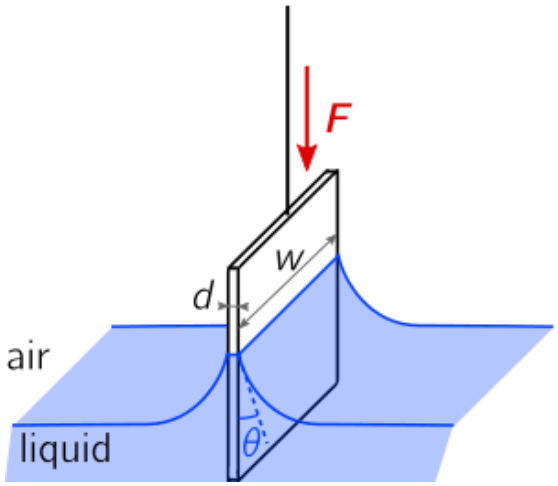

Figure 3.3 Working of Whilhelmy Plate Tensiometer

A Platinum plate is desired for measuring the SFT or IFT as it is chemically inert and has high melting point. Because of this property it doesn't get melted and hence can be burnt again and again after each experiment which is a necessary. Another important of selecting this plate is that as it can be optimally wetted on account of its very high surface free energy it generally forms a contact angle θ of 0° ($\cos\theta = 1$) with liquids. The required variable γ can be calculated directly from the measured force. Unlike the du Nouy ring method which follows a quasi – static ring method in this method the surface remains static during carrying out measurements. Concurrent readings were obtained over a period of time and an average value is taken of all the surface tension values.

The platinum plate was fully rinsed with water followed by alcohol and burnt before and after each measurement to remove the impurities, if any.

3.3.2 Rheological Measurements

All rheological measurements were performed by stress controlled TA HR-2 Discovery Hybrid Rheometer. The cone and plate geometry was used for all the rheological studies which has 40 mm cone diameter and cone angle (deg: min: sec) 2: 0: 25. This type of geometry is generally used because cleaning is quite easy, doesn't require large sample volumes and with a proper handling it can be used on materials having a viscosity to about ten times that of water (10 mPa.S) or even lower. The range of shear rate for steady shear viscosity measurements was from 0.01 to 300 s^{-1}. Frequency from 0.1 to 100 rad/s was applied for oscillatory measurements. All reported data points are within torque limits (±5 mNm−2000 mNm) .Since the values of strain and shear rate are dependent on angular

displacement and the gap, it follows that the smaller the cone angle, the greater the error is likely to be in gap setting and hence your results. When a geometry of large angles is used (4° or 5°) it becomes easier to get reproducibility of gap setting but the larger the cone angle more variations in the shear rate across the gap is observed. Hence an intermediate value was selected for all the measurements. Basically when the plate is rotated, the force on cone measured. Cone dimensions and Rotational speed give the shear rate. This Rheological characterization includes the determination of relative viscosity, shear rate and shear stress relationship at different concentrations of surfactant concentrations.
All the experiments were carried out at 25˚C.

3.4 Preparation of solutions

3.4.1 Preparation of stock solutions of surfactants and electrolytes:

The surfactants, CTAB and IGEPAL CO 890 were obtained from Sigma Aldrich Company. Different solutions with a molar concentration of 10 mmol having a ratio (CTAB to IGEPAL) of 0:10, 3:7, 7:3, 10:0 solutions were prepared by adding required amount of surfactants to a specific volume of water in a beaker. The beakers were sonicated in a sonicator till the solutes completely dissolve and they were transferred into a volumetric flask and the total volume is made up to 50ml.

The electrolytes, NaCl and Na_2SO_4 were obtained from RANKEM Chemicals and NaH_2PO_4 was obtained from Merck Millipore. Different solutions of each of the electrolytes with molar concentration of 150mmol were prepared by adding required amount of electrolytes to a specific a volume of water in a beaker. The beakers were sonicated at a high frequency in a sonicator till the solutes completely dissolve. Later they were transferred into a volumetric flask and the total volume is made up to 50ml.

3.4.2 Preparation of CarboxyMC (Carboxymethyl Cellulose) solutions:

Carboxymethyl cellulose with a viscosity range of 2-4 centipoise, used in the present work was supplied from Loba Chemie Chemical Company. Aqueous solutions of 2 wt% cellulose were prepared by dissolving the appropriate amount of cellulose in distilled water at room temperature and kept in vials. To study the effect of surfactants, different molar concentrations of above prepared surfactants ranging from values below CMC (0.01 mmol),

at CMC as well as above CMC (4 times CMC) were added with the required amount of cellulose in different vials to maintain 2 wt%. To study the effect of electrolytes on cellulose, different solutions were prepared by adding 150 mmol of three different electrolytes along with the surfactants at 0.01mmol, maintaining 2wt% of cellulose in the solution. Previous tests showed that the preparation of solutions requires a minimum time to fully dissolve the cellulose powder. This time depends on the polymer concentration as well as stirring time. No external power or heat was supplied for mixing as it may disrupt the polymerized structure of the solution.

Chapter 4

RESULTS AND DISCUSSION

4.1 CMC values of mixed surfactants :

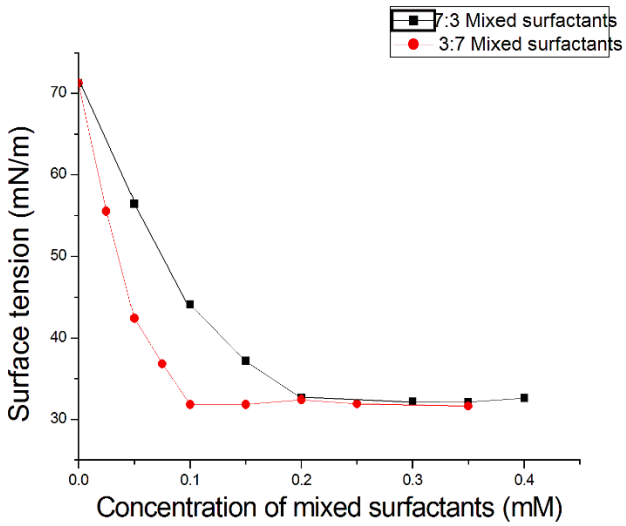

Fig 4.1 Surface tension versus concentration graph of mixed surfactant systems (7:3 and 3:7 molar concentrations)

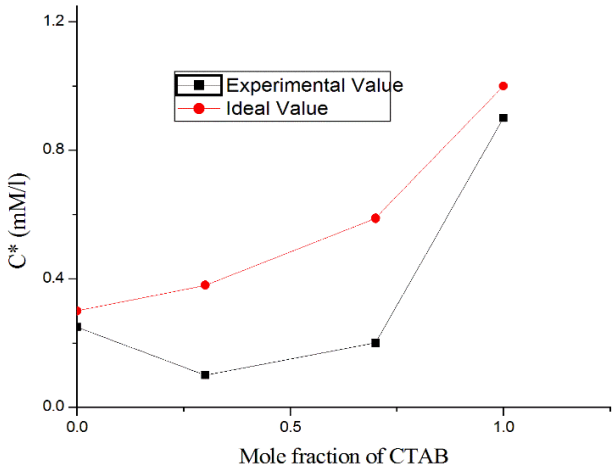

Fig 4.2 CMC value of mixed surfactants system (7:3 and 3:7 molar concentrations)

The CMC values obtained for mixed surfactant solutions of CTAB and IGEPAL CO 890 as a function of the mole fraction of CTAB are shown in the Fig. It is observed that mixed CMC values obtained experimentally are lower than those obtained by assuming ideal behaviour. The experimental results also shows that for 7:3 molar ratio of mixed surfactants the CMC is higher than that of 3:7 molar ratio of mixed surfactants. The most mechanistic reason for the reduction of CMC value is because of the reduction in repulsion between ionic heads due to

the insertion of non-ionic heads in between them. On addition of non-ionic surfactants the process of aggregation is facilitated as there is an absence of non-ionic surface active agents, hence the CMC values are much lower than those ionic surface active agents. As far as the effect of number of hydrophilic groups are concerned, increase in the number of any hydrophilic group increases the solubility of surface active agents, leading to increase in CMC. The interaction parameter (β) was calculated using Rubingh's equation of regular solution theory as mentioned below:

$$\frac{x^2 \ln(\frac{\alpha_1 C_{12}}{x_1 C_1})}{(1-x)^2 \ln(\frac{(1-\alpha_1) C_{12}}{(1-x_1) C_2})} = 1 \quad (3)$$

$$\beta = \frac{\ln(\frac{\alpha_1 C_{12}}{x_1 C_1})}{(1-x)^2} \quad (4)$$

Surface Excess can be calculated as

$$\Gamma = \frac{2.303 RT d\gamma}{d \log C} \quad (5)$$

Area per molecule can be calculated as

$$A = \frac{10^{20}}{\Gamma N_0} \quad (6)$$

An attractive interaction between the different surfactant molecules of the mixed micelle has been observed of which the negative values of β parameter is the justification. The β parameter is more negative (-6.667) for the 3:7 mixed solution because of the higher synergistic effect, and as a result the surface excess is maximum γ_{cmc} and the area occupied by the surfactant molecules at the air water interface are minimum among both the mixing ratios studied here.

Table 4.1 Values of surface tension, interaction parameter, critical micelle concentration (CMC), surface excess, and area occupied per surfactant molecule for pure and mixed surfactant solutions

Mole fraction (CTAB)	CMC (experimental)	CMC (Theoretical)	Interaction parameter (β)	Surface Tension (y)	Surface Excess $\Gamma_{max}*10^{-6}$ (mole m^{-2}) of CTAB	Area per molecule (nm^2)
0	0.25	0.3	-	38.11	2.60	0.63
0.3	0.1	0.38	-6.667	31.815	1.67	0.99
0.7	0.2	0.588	-4.36	32.612	1.59	1.04
1	0.9	1	-	32.75	1.70	0.96

However, at the 7:3 ratio, the interaction parameter is less negative (−4.36) and the surface area occupied by the surfactant molecules is maximum (1.04 nm^2). The correct reason for the loose packing at the 7:3 composition is not clear, but attributed to a less synergistic interaction because of the presence of lesser amount of non-ionic surfactant.

4.2 Effect of electrolytes on CMC values of surfactants:

The effect of different electrolytes NaCl, Na_2SO_4 and NaH_2PO_4 has been studied at two surfactant concentrations 0.001 and 0.01 mmol and the reduced values of CMC were obtained and plotted in the graph below in Figure 4.3 , 4,4 and 4.5. The results show that in the presence of electrolytes, there are further decreases in surface tension with increasing electrolytes concentration compared to the mixed solutions without the electrolyte. For a fixed concentration of surfactant mixture with the increasing electrolyte concentration, in the presence of a tri-valent counter-ion (PO_4^{3-}), decrease in the surface tension and contact angle are more compared to the mono-valent (Cl^-) and di–valent (SO_4^{2-}). It was observed that the CMC values for a constant surfactant concentration is lowest for NaH_2PO_4 while for NaCl and Na_2SO_4 the values were found to be almost same. The ultimate surface tension value becomes constant at a certain electrolyte concentration for three different concentrations of

mixed surfactants tested here, but the plateau values and the required electrolyte concentration decrease with increasing total mixed surfactant concentration.

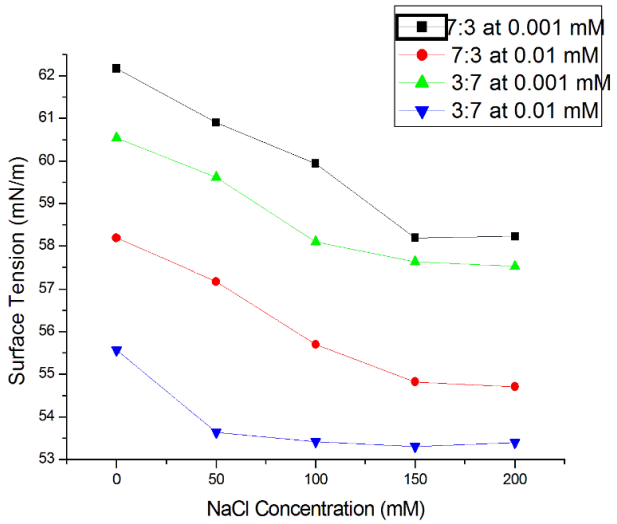

Fig 4.3 Plot of surface tension vs NaCl electrolyte concentration in 7:3 and 3:7 molar ratio for three different mixed surfactant concentration

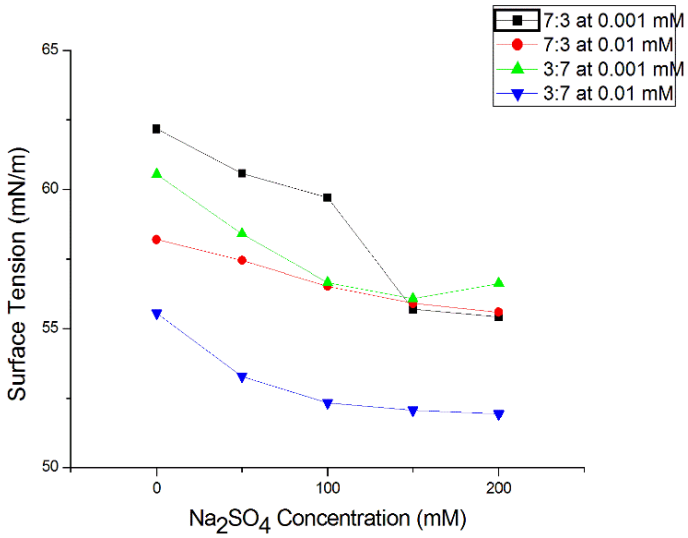

Fig 4.4 Plot of surface tension vs Na_2SO_4 electrolyte concentration in 7:3 and 3:7 molar ratio for three different mixed surfactant concentration

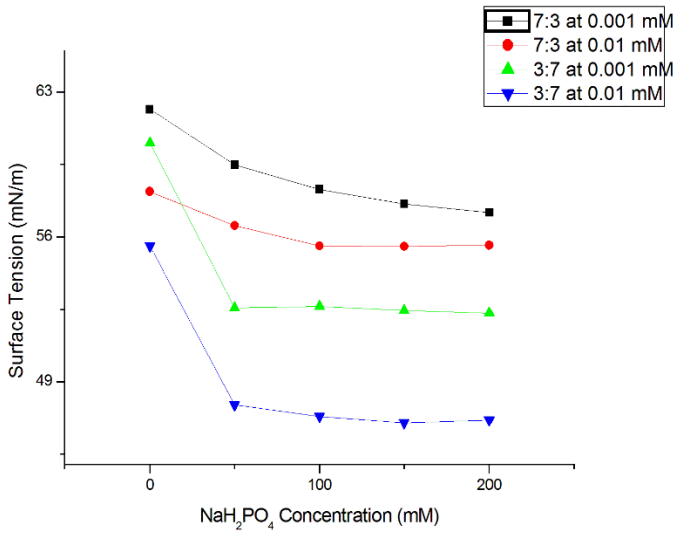

Fig 4.5 Plot of surface tension vs NaH_2PO_4 electrolyte concentration in 7:3 and 3:7 molar ratio for three different mixed surfactant concentration

As an example, for 3:7 and 0.001 mM surfactant concentration in the presence of 200 mM NaCl, the ultimate surface tension is 57.522 mN m^{-1}, whereas in the presence of 200 mM Na_2SO_4 and NaH_2PO_4, those values reduce to 56.625 mN m^{-1} and 52.327 mN m^{-1} respectively. When the surfactant concentration is ten times higher (0.01 mM), the surface tension decreases to the values of 53.393 mN m^{-1} at 200 mM NaCl, whereas they are 51.933 mN m^{-1} and 47.153 mN m^{-1} at the same concentration of Na_2SO_4 and NaH_2PO_4 respectively; however, these saturation values are still higher compared to the values at the CMC (0.2 mM) of the same surfactant composition without any electrolyte solution. This can be attributed to the fact that at a very low surfactant concentration, even in the presence of a high electrolyte concentration, the adsorption of surfactant molecules at the interfaces could not reach the saturation level. Hence, from these results it can be concluded that the decrease in value of surface tension in the presence of electrolytes is mainly because of the reduction in the repulsive force between the surfactant head groups by the counter-ions of the electrolytes at both the interfaces. The valency of the counter-ion is another important factor that leads to the decrease in the surface tension, as the effective charge density is high for the higher-valency ions, which in turn greatly reduces the requirement of electrolytes to screen the charge of the surfactant head groups. The most mechanistic reason for the reduction of CMC value is because of the reduction in repulsion between ionic heads due to the insertion of nonionic heads in between them.

4.3 Basic Flow Curves :

4.3.1 Relationship Between Shear Stress and Shear Rate:

- **Effect of mixed surfactant :**

Figure 4.6 and Figure 4.7 show the relationship between stress and applied shear rate of Carboxymethyl Cellulose in the presence of mixed surfactants systems. The value of shear rate was initially increased from 0 to 280 1/s and then decreased again to zero to study the extent of reformation of the internal structure which was damaged due to application of varying shear rate. Hence, the area ($Area_{in}$) between the plateau regions of both increasing as well as decreasing value of shear rate was calculated for each sample and was shown in the graph.

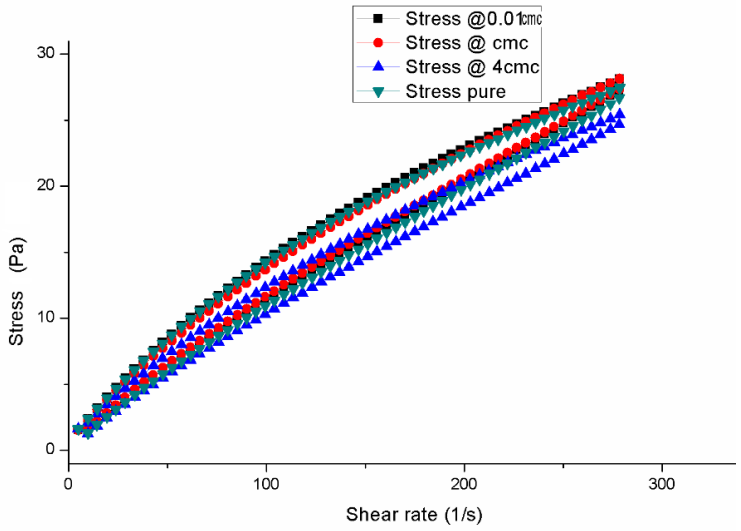

Fig 4.6 Variation of Shear Stress with shear rate of 7:3 mixed surfactant system (A_{in} @0.01 cmc -621unit^2 @cmc-459 unit^2 @4cmc-445.5458 unit^2 @pure- 672.8055 unit^2)

In all cases, when the shear rate is slowed, the stress path lags forming a hysteresis loop, which then returns to a point lower than the initial critical shear stress. The area within the hysteresis loop represents the energy consumed in structure breakdown. From both the graphs it was observed that the extent of reformation of internal structure increases on addition of more surfactant as a decrease in the $Area_{in}$ is observed and it is highest for pure Carboxymethyl cellulose indicating weak internal structure.

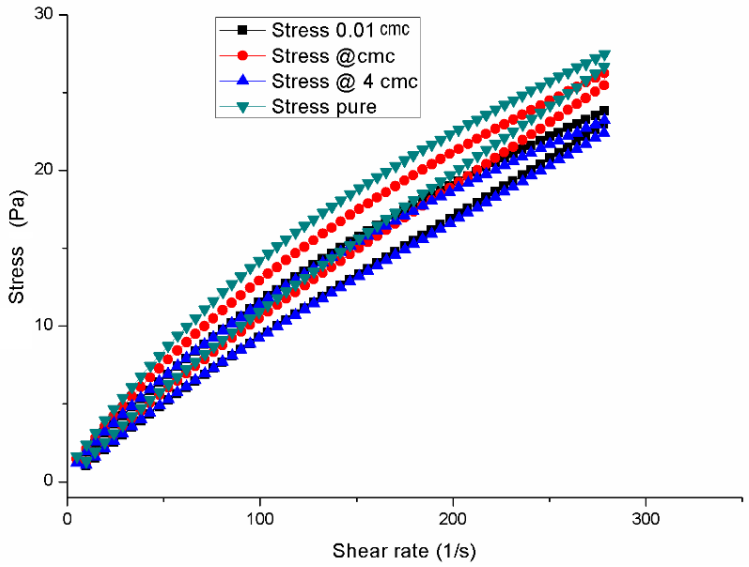

Fig 4.7 Variation of Shear Stress with shear rate of 3:7 mixed surfactant system (A_{in} @0.01 cmc -511unit^2 @cmc-529.55 unit^2 @4cmc-486.567 unit^2 @pure- 672.8055 unit^2)

This observation is due to the fact that with increase in surfactant concentration hydrophobic interaction between the surfactant molecules and the cellulose hydrophobes increases and hence it builds up a compact and stable internal structure due to which it exhibits more extent of reformation of internal strength when shear rate is decreased. Comparing both the mixed surfactant systems 7:3 system exhibits higher strength recovery than that of the 3:7 as $Area_{in}$ is lesser for 7:3 than 3:7 mixed surfactant systems.

- **Effect of Electrolyte:**

On addition of different electrolytes i.e. NaCl, Na_2SO_4 and NaH_2PO_4 the reforming strength is more enhanced when compared to samples without electrolytes and this was clearly shown in Fig 4.8 and Fig 4.9. This observation can be attributed to the formation of 'mixed' micellar junctions comprising of both polymer and surfactant hydrophobes resulting in the strengthening of the hydrophobic junctions.

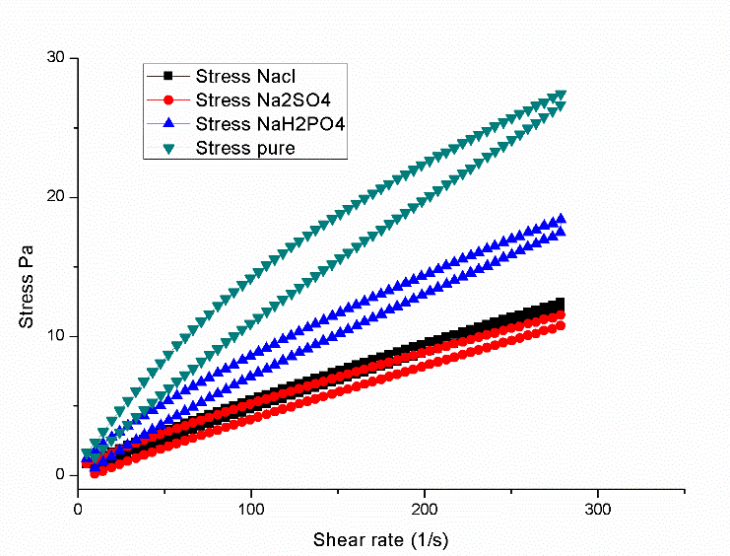

Fig 4.8 Variation of shear stress with shear rate of 7:3 mixed surfactant system with 150 mmol concentration of different electrolytes (A_{in} @NaCl - 179.146unit^2 @Na_2SO_4 -277.271 unit^2 @NaH_2PO_4 -370.66 unit^2 @pure- 672.8055 unit^2)

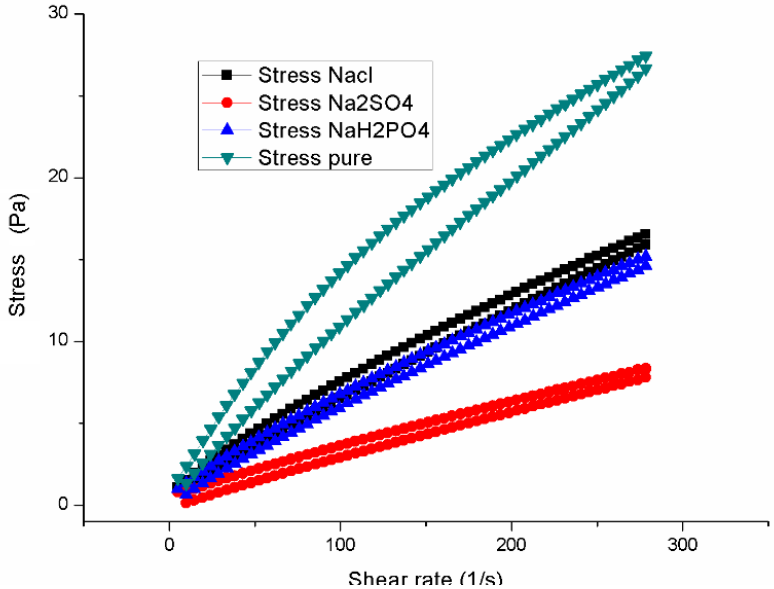

Fig 4.9 Variation of shear stress with shear rate of 3:7mixed surfactant system with 150 mmol concentration of different electrolytes (A_{in} @NaCl -259.498 unit^2 @Na_2SO_4 -186.32 unit^2 @NaH_2PO_4 205.44 unit^2 @pure- 672.7131 unit^2)

Although there is a reverse trend observed i.e. with increase in the valency of electrolyte the $Area_{in}$ increases significantly in 7:3 surfactant systems where as the increase is lesser in 3:7

mixed surfactant system. This can be associated with the fact that with increase in valency of electrolytes the charge density increases and it is more in 7:3 mixed surfactant system due to the presence of more fraction of cationic surfactant and hence more repulsive electrostatic interaction occurs between the charged particles and the counter ions which results in a disrupted and weak internal structure. Hence on reducing the shear rate the reforming stress values in 7:3 were not found to be near the values of those of increasing rates.. The values of the area were tabulated in the following table 4.2.

Table 4.2 Calculation of Hysteresis Area

System		Variable Parameters	Hysteresis Area (sq. unit)
7:3 (CMC = 0.2mM)	With electrolyte	NaCl	179.14647
		Na_2SO_4	277.27
		NaH_2PO_4	370.66
	Without electrolyte	0.01 mM surfactant	621.72
		At 1 CMC surfactant	459.65
		At 4 CMC surfactant	445.55
		Pure Cellulose	672.80
3:7 (CMC = 0.1mM)	With electrolyte	NaCl	255.49
		Na_2SO_4	186.317
		NaH_2PO_4	205.44
	Without electrolyte	0.01 mM surfactant	511.101
		At 1 CMC surfactant	519.55
		At 4 CMC surfactant	486.57
		Pure Cellulose	672.8

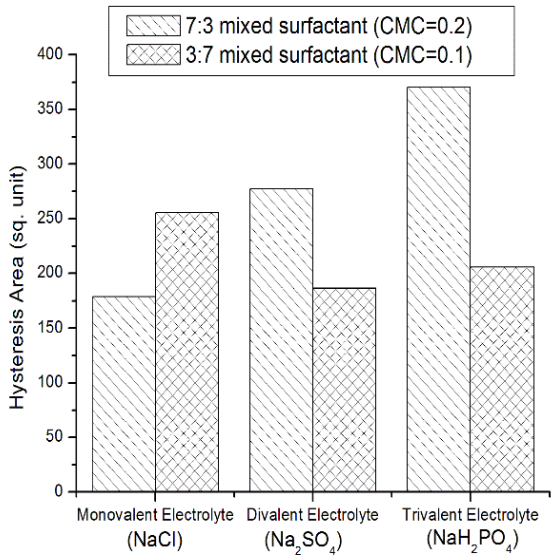

Fig 4.10 Bar representation of hysteresis area in the presence of electrolytes for both the ratios of surfactants

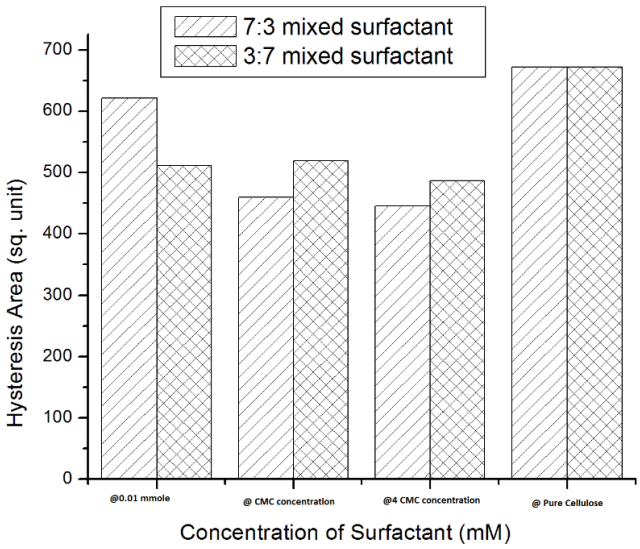

Fig 4.11 Bar representation of hysteresis area in the absence of electrolytes for both the ratios of surfactants

The corresponding areas $Area_{in}$ in presence and absence of the electrolytes were plotted in bar graphs Fig 4.10 and 4.11.

4.3.2 Effect of shear rate on viscosity :

- **Effect of mixed surfactant:**

The effect of mixed surfactants system on Carboxymethyl cellulose was studied in a controlled TA HR-2 Discovery Hybrid Rheometer with cone and plate geometry. The effect of shear rate on viscosity of cellulose was studied by gradually increasing the shear rate from 0 to 200 1/s and the values were plotted on graphs as shown in Figure 4.12 and 4.13. It was observed that for both the types of surfactants i.e. 3:7 as well as 7:3 surfactant systems at different molar concentrations, the apparent viscosity of cellulose at low shear rate exhibits rather high values, which is related to the three-dimensional network structure and decreases with the increase in shear rate values. The occurrence of the maximum viscosity is due to higher content of polymer segments in the mixed surfactant aggregates with a few surfactant monomers.

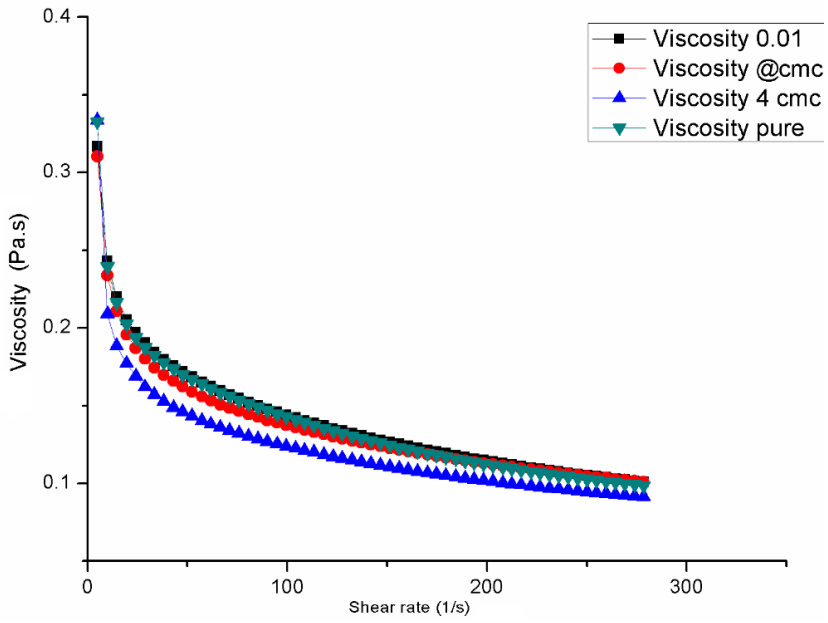

Fig 4.12 Variation of Viscosity with shear rate of 7:3 mixed surfactant system

As shown in the curves, after being immersed into surfactant solutions, the apparent viscosity of cellulose at a lower shear rate decreases with the increase of surfactant concentration compared with the unimmersed one.

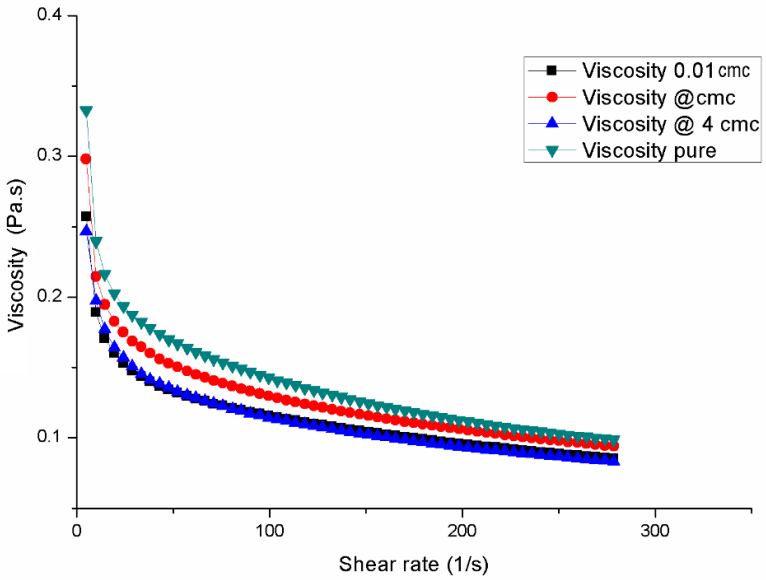

Fig 4.13 Variation of Viscosity with shear rate of 3:7 mixed surfactant system

The subsequent decrease in the viscosity with increasing surfactant concentration indicates that the aggregate formation results in a more compact polymer structure due to reduction in the level of entanglement or cross linking as the polymer substituent groups redistribute in the increasing number of aggregates. The three dimensional network structure of viscoelastic cellulose is destroyed at higher shear rate, and cellulose exhibit shear-thinning, too. Therefore, at higher shear rate, the apparent viscosity of cellulose immersed in surfactant solutions with different surfactant concentrations hardly changed. It is noted that the viscosity is highest for molar concentration at CMC value as compared to other surfactant concentrations values. This result can be attributed to the fact that up to a certain value of surfactant the molecules remain intact and when more surfactant molecules were added the cellulose structure starts to dissociate and it starts rearranging with surfactant molecules. From the graph it was observed that the viscosity values for 7:3 molar concentrations is comparatively higher than that of 3:7 molar concentrations. This can be attributed to the fact that is due to the fact that in the later mixed surfactant system surfactant micelles may have higher saturating effect on the polymer hydrophobes, hindering its association with other

polymer hydrophobes thereby leading to a decrease in network connectivity and hence, viscosity.

- **Effect of Electrolyte:**

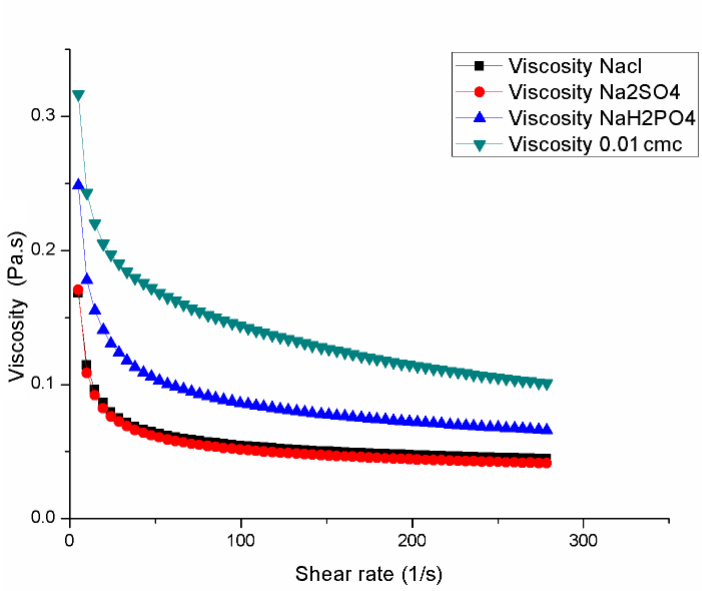

Fig 4.14 Variation of Viscosity with shear rate of 7:3 mixed surfactant system with 150 mmol concentration of different electrolytes

Figure 4.14 and Figure 4.15 show the effect of various electrolytes on the viscosity of Carboxymethyl Cellulose. It was observed that the viscosity values were quite lower than that of the pure Carboxymethyl Cellulose. This can be attributed to the fact that addition of electrolytes brings counterions in the system which reduces the stretching in polymer chains by charge screening and resulting in reduction in viscosity.

It is also interesting to note that viscosity is lowest in the whole range of shear rate values for NaCl in both the mixed surfactant systems as compared to other electrolytes. This is due to the fact that NaH_2PO_4 and Na_2SO_4 being higher valency electrolytes when mixed with Carboxymethyl cellulose induces higher charge density around the complex molecules.

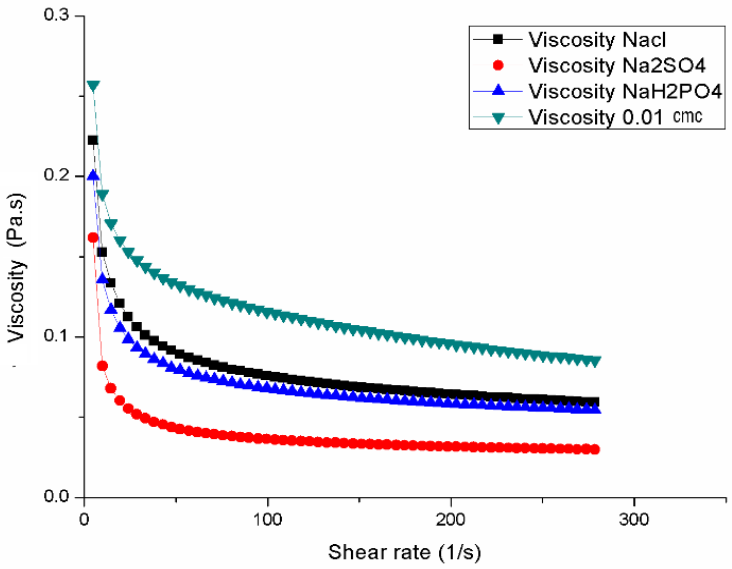

Fig 4.15 Variation of Viscosity with shear rate of 3:7 mixed surfactant system with 150 mmol concentration of different electrolytes

Due to the higher charge density the surfactant molecules may not adsorb between the cellulose hydrophobes and hence higher interactions between the cellulose molecules is observed which results in higher viscosity.

Chapter 5

CONCLUSION

CONCLUSION AND FUTURE WORK:

Study of mixed surfactants was done in the absence and presence of electrolytes and different properties such as CMC values, interaction parameters, surface excess area and particle area were observed. As the CMC and surface tension values of mixed surfactants were found to be lower than that of the individual values they can be used in a wide range of applications. As cationic surfactants are more economical in comparison to that of non-ionic surfactants a ratio of 7:3 was found to be better than that of 3:7 molar concentration although the later mixed surfactant system has lower CMC. Flow Rheological studies of Carboxymethyl cellulose was also studied in the presence of mixed surfactants and electrolytes and a significant change in viscosity as well the internal structure due to additives were observed. The presence of surfactants improves the structured network of cellulose where as higher valency electrolytes somewhat disrupts the network due to higher charge density.

A lot of further studies can be done on the rheological properties of cellulose as well as the physicochemical properties of mixed surfactants as they present a lot of scopes and applications in a wide range of areas. As this report is limited to only cationic and anionic surfactants, different other types of surfactants can be used and their surface properties can be determined. Time dependent rheological measurements as well as creep flow measurements of Carboxymethyl cellulose so as to have a depth knowledge regarding the internal structure of the cellulose complex in presence of surfactants and electrolytes.

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